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MERCURATION OF NITROHYDROXYBENZALDEHYDES.

BY

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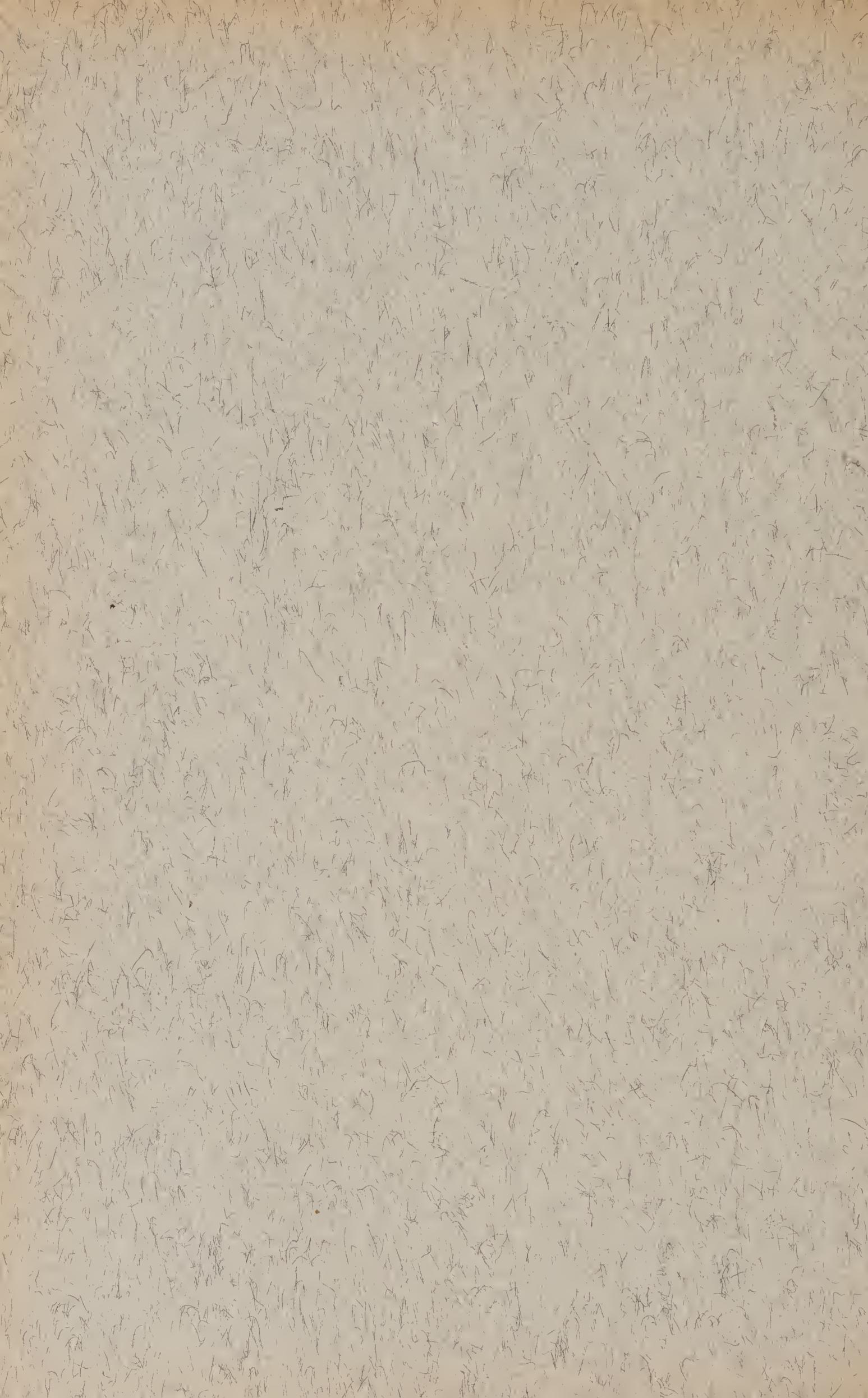


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CXXI.—*Mercuration of Nitrohydroxybenzaldehydes.*

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IN a previous paper (J., 1922, **121**, 1055) mercury compounds derived from the three hydroxybenzaldehydes were described and their constitution established * except as regards the acetoxy-mercuri-*m*-hydroxybenzaldehyde. It is now shown that the mercury in this substance must be in position 2, with respect to the aldehyde group, since on its replacement by the nitro-group there is formed the known 2-nitro-3-hydroxybenzaldehyde and similarly when the mercury residue is replaced by iodine, the iodo-*m*-hydroxybenzaldehyde produced is convertible, by heating with sodium hydroxide solution, into 2 : 3-dihydroxybenzoic acid.

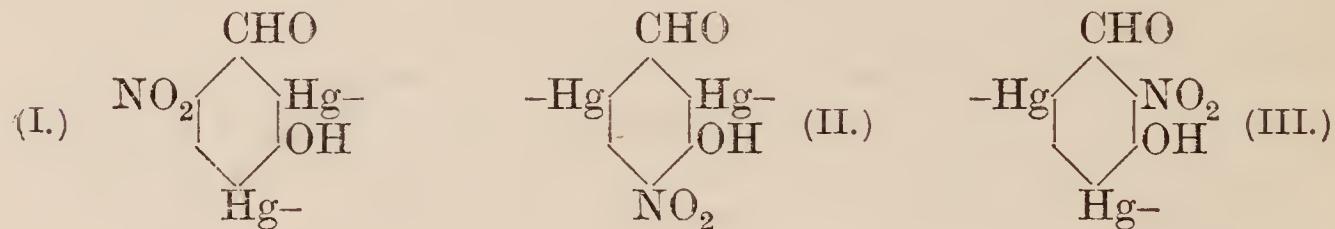
This work has now been extended to the nitro- and nitrohydroxybenzaldehydes. None of the three mononitrobenzaldehydes yields mercury derivatives even when boiled in solution with mercuric acetate for three weeks. The *m*-compound when boiled with mercuric acetate and sodium hydroxide is oxidised to *m*-hydroxybenzoic acid, m. p. 140—143° (corr.) [aniline salt, m. p. 115—116° (corr.)]. The nitrohydroxybenzaldehydes † on the contrary are readily mercurated. 3-Nitro-4-hydroxybenzaldehyde when boiled in 50 per cent. alcoholic solution with one molecular proportion of mercuric acetate yields only 5-hydroxymercuri-3-nitro-4-hydroxybenzaldehyde. The three known mononitro-3-hydroxybenzaldehydes each yield both mono- and di-mercuri-derivatives, which

* The melting point of 3 : 5-diacetoxydimercurisalicylaldehyde by a clerical error was given as 133° (decomp.) instead of 233° (decomp.; corr.) in the previous paper.

† The mercuration of nitro-*o*-hydroxybenzaldehydes has already been investigated by Whitmore and Middleton (J. Amer. Chem. Soc., 1923, **45**, 1330).

can be separated by fractional crystallisation from appropriate fatty acids; if the mercuric acetate is increased to two molecular proportions the product consists almost entirely in each case of the corresponding dimercuri-derivative, very little of the mono-compound being formed.

In such compounds, the mercury can usually be replaced by a nitro-group or by a halogen, and it has been assumed generally that the group thus introduced occupies the same position in the molecule as the mercury it replaces, and it is on this basis that constitutional formulæ have been assigned to many of the organic derivatives of mercury already described. The results obtained in applying such processes to the dimercurinitro-*m*-hydroxybenzaldehydes show that the assumption is not always justified. Thus the dimercuri-compounds formed from the 6-nitro-, 4-nitro-, and 2-nitro-derivatives of *m*-hydroxybenzaldehyde all yield on treatment with bromine, 2:4-dibromo-6-nitro-3-hydroxybenzaldehyde. This substance should be produced from the 6-nitro-derivative (I)*, whereas the 4-nitro-isomeride (II) should yield 2:6-dibromo-4-nitro-3-hydroxybenzaldehyde and the 2-nitro-isomeride (III) ought to furnish 4:6-dibromo-2-nitro-3-hydroxybenzaldehyde.



The steps taken to ensure the purity and identity of the initial materials, proof that the three dimercuri-compounds are different, and evidence of the identity and constitution of the single dibromo-nitro-*m*-hydroxybenzaldehyde yielded by the three are detailed in the experimental portion and need not be summarised here. The authors are of opinion that the data given leave no room for doubt that in the action of bromine on the two dimercuri-compounds formed from the 2-nitro- and 4-nitro-*m*-hydroxybenzaldehydes each nitro-group changes position with the bromine atom, which replaces the mercury atom in position 6.

This anomalous behaviour with bromine made it difficult to determine the position of the mercury residues in the 4-nitro- and 2-nitro-derivatives and it has not been found possible to replace mercury in these substances by nitro-groups. Fortunately, they behave normally with iodine and with the assistance of the results

* In these formulæ, Hg- represents a mercuri-residue -HgOH, -HgOAc, etc.

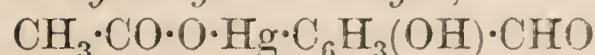
of this reaction it has been possible to suggest the three formulæ already given for these products.

The monomercuri-derivatives of all three nitro-compounds have been obtained, but only in small amounts and although each yields, on replacement of the mercury by iodine, a characteristic iodo-compound, none of these is known and the quantities obtainable so far have precluded the determination of the position of the iodine, and therefore also of the mercury in the original compounds, although it is probable that the mercury residue is in each case ortho- to the hydroxyl group.

As in the case of the mercurated hydroxybenzaldehydes described in the previous paper, the bactericidal action of these new compounds has been determined by Major Brown, C.I.E., M.B., B.Ch., of the Wellcome Bureau of Scientific Research, who finds that *Bacillus typhosus* is killed in 5 minutes by solutions containing (a) 0.004 per cent. of chloromercuri-4-nitro-3-hydroxybenzaldehyde, (b) 0.06 per cent. of either the 2 : 4-dihydroxydimercuri-6-nitro- or 4 : 6-dihydroxydimercuri-2-nitro-derivative of *m*-hydroxybenzaldehyde, (c) by amounts intermediate to these of the other mercury derivatives of *m*-hydroxybenzaldehyde, or (d) 0.12 per cent. of the 5-hydroxymercuri-3-nitro-derivative of *p*-hydroxybenzaldehyde. For these bactericidal trials, the compounds were used in the form of potassium salts.

EXPERIMENTAL.

2-Acetoxymercuro-3-hydroxybenzaldehyde,



(J., 1922, **121**, 1059).—When a molecular mixture of this substance with potassium nitrate is added to sulphuric acid cooled below 0°, a small yield of 2-nitro-3-hydroxybenzaldehyde is obtained, identical, as shown by determination of the mixed melting point, with that prepared by Friedländer and Schenck's method (Ber., 1914, **47**, 3043).

The iodo-3-hydroxybenzaldehyde obtained from the same mercury compound by the action of iodine in potassium iodide (*loc. cit.*), when heated at 100° with a 50 per cent. aqueous solution of sodium hydroxide, furnishes a small yield (accompanied by much dark brown acid resin) of an acid melting at 203°, which gives an insoluble lead salt, a blue colour with ferric chloride, changing to red on addition of sodium bicarbonate, and when mixed with recently ignited ground pumice stone and heated yields a crystalline sublimate having the characters of catechol (m. p. 103—104°, green colour with ferric chloride). The 2 : 3- and 3 : 4-dihydroxybenzoic acids are the only acids likely to yield catechol in this way, and of

these the 3 : 4-dihydroxybenzoic acid (protocatechuic acid) depresses the melting point of the acid under discussion to 166°. All the reactions of the latter acid are characteristic of 2 : 3-dihydroxybenzoic acid, and the authors have no doubt they are identical, although combustions of their acid did not give good results (Found : C = 55.6, 55.9; H = 4.12, 4.12. Calc., C = 54.5; H = 3.9 per cent.) owing to the difficulty of removing the last traces of the accompanying brown resin from the small total quantity of acid obtained. This iodo-*m*-hydroxybenzaldehyde undergoes decomposition with remarkable ease, and of the reactions tried with a view to its identification only the above has given a useful product, and that in a yield less than 2 per cent. of the theoretical.

In view of the production from it, as just described, of 2-nitro-3-hydroxybenzaldehyde and 2 : 3-dihydroxybenzoic acid, the original mercury compound must be 2-acetoxymercuri-3-hydroxybenzaldehyde.

Mercuration of Nitrohydroxybenzaldehydes.

The mercuration was effected in the same way throughout, namely, by boiling under reflux the nitrohydroxybenzaldehyde (1 mol.) with mercuric acetate (1 mol. or 2 mols.) in 50 per cent. alcohol containing a little acetic acid, boiling being continued until the mixture dissolved completely on adding sodium hydroxide solution.

The 3-nitro-4-hydroxybenzaldehyde used was prepared by Paal's method (*Ber.*, 1895, **28**, 2415); the yield obtained was 70 per cent. of the 4-hydroxybenzaldehyde used and the melting point was, as recorded, 141—142°.

5-Hydroxymercuri-3-nitro-4-hydroxybenzaldehyde,



—This substance, obtained in quantitative yield by the general method, separates from the boiling solution in microscopic, orange platelets, which darken at about 285°, but do not melt at 300°. It is purified by solution in sodium hydroxide, in which it dissolves to form a deep orange-red liquid, and precipitation with carbon dioxide (Found : Hg = 52.46; N = 3.76. $\text{C}_7\text{H}_5\text{O}_5\text{NHg}$ requires Hg = 52.29; N = 3.65 per cent.). Addition of dilute hydrochloric acid to such a solution causes the precipitation of 5-chloromercuri-3-nitro-4-hydroxybenzaldehyde, which crystallises from alcohol in tufts of minute, colourless needles, m. p. 226° (decomp.; corr.) (Found : Hg = 49.77. $\text{C}_7\text{H}_4\text{O}_4\text{NClHg}$ requires Hg = 49.89 per cent.). The hydroxymercuri-compound is insoluble in the usual solvents except glacial acetic acid, from which there slowly separate colourless prisms of 5-acetoxymercuri-3-nitro-4-hydroxy-

benzaldehyde (Found : Hg = 47.15. $C_9H_7O_6NHg$ requires Hg = 47.13 per cent.). This darkens on heating at about 250° , but does not melt at 300° .

On shaking the finely powdered hydroxymercuri-compound with excess of a 5 per cent. solution of iodine in potassium iodide, the mercury is removed as mercuric iodide and a quantitative yield of the sparingly soluble (in potassium iodide) potassium salt of an *iodo-3-nitro-4-hydroxybenzaldehyde* is obtained. The free phenol crystallises from chloroform in yellow plates, m. p. $171-172^\circ$ (corr.) (Found : C = 28.82, 28.30; H = 1.58, 1.97; N = 4.64; I = 43.38. $C_7H_4O_4NI$ requires C = 28.68; H = 1.37; N = 4.78; I = 43.33 per cent.). On oxidation with alkaline permanganate it is converted into 5-iodo-3-nitro-4-hydroxybenzoic acid, m. p. 247° (decomp.; corr.) (Found : I = 41.02. Calc., I = 41.08 per cent.), alone or mixed with a specimen prepared by Gerland's method (*Annalen*, 1854, **91**, 192). Kharasch (*J. Amer. Chem. Soc.*, 1921, **43**, 1204) gives the melting point as 251° .

The mercury compound formed from 3-nitro-4-hydroxybenzaldehyde must therefore be 5-hydroxymercuri-3-nitro-4-hydroxybenzaldehyde.

6-Nitro-3-hydroxybenzaldehyde was obtained, along with 4-nitro-3-hydroxybenzaldehyde and 2-nitro-3-hydroxybenzaldehyde, by nitrating *m*-hydroxybenzaldehyde according to Pschorr's process (*Ber.*, 1901, **34**, 4400) and separating the isomerides by Fricdländer and Schenck's method (*loc. cit.*). When crystallised from benzene, they have the following characteristics, the figures in parenthesis being the melting points recorded by Friedländer and Schenck :— 6-Nitro-3-hydroxybenzaldehyde, long, thin, yellow needles, m. p. $170-171^\circ$ (166°); 4-nitro-3-hydroxybenzaldehyde, thick, four-sided, yellow plates, m. p. 134° (128°); 2-nitro-3-hydroxybenzaldehyde, small, colourless prisms, m. p. 157° (152°). These characteristic forms invariably separate from any mixture crystallised slowly from benzene.

When molecular proportions of 6-nitro-3-hydroxybenzaldehyde and mercuric acetate are treated by the general method, an orange-coloured solid (A), which consists wholly of dimercurated products, separates from the boiling solution and is filtered off hot at the end of the reaction. On cooling and concentrating the filtrate, further amounts of solid, lighter in colour and consisting of mixtures of mono- and di-mercurated products along with unchanged 6-nitro-3-hydroxybenzaldehyde, are obtained.

The solid (A) appears to be a mixture of diacetoxydimercuri- and dihydroxydimercuri-compounds (Found : Hg = 64.12; N = 2.24. $C_{11}H_9O_8NHg_2$ requires Hg = 58.62; N = 2.05. $C_7H_5O_6NHg_2$

requires $Hg = 66\cdot83$; $N = 2\cdot33$ per cent.). It is insoluble in the usual organic solvents, but dissolves in formic, acetic, propionic, or *n*-butyric acid, and is best purified by solution in propionic acid, from which it separates as orange-yellow needles of *2:4-dipropionoxydimercuri-6-nitro-3-hydroxybenzaldehyde* (the propionoxymercuri-group = $-HgO\cdot CO\cdot C_2H_5$) (Found: $Hg = 56\cdot26$. $C_{13}H_{13}O_8NHg_2$ requires $Hg = 56\cdot32$ per cent.) exploding at 235° (corr.). This substance is sparingly soluble in sodium hydroxide solution to an orange-coloured liquid (the solid itself is coloured bright red by alkalis) which is decomposed by hydrochloric acid with precipitation of *2:4-dichlorodimercuri-6-nitro-3-hydroxybenzaldehyde*; the latter crystallises from alcohol in colourless, microscopic needles (Found: $Hg = 57\cdot97$; $N = 2\cdot14$; $Cl = 10\cdot56$. $C_7H_3O_4NCl_2Hg_2 + 3H_2O$ requires $Hg = 58\cdot03$; $N = 2\cdot03$; $Cl = 10\cdot26$ per cent.).

The monomercurated compound is obtained from the more soluble fractions of the mixture by extracting the finely ground substance with ether to remove unmercurated material, dissolving the residue in potassium hydroxide solution, and precipitating with hydrochloric acid. The pale yellow solid thus obtained is crystallised from alcohol, whence *monochloromercuri-6-nitro-3-hydroxybenzaldehyde* is easily obtained (Found: $Hg = 49\cdot98$. $C_7H_4O_4NClHg$ requires $Hg = 49\cdot89$ per cent.). It decomposes at 198° (corr.).

The dimercurated compound on agitation with a cooled, freshly prepared 5 per cent. solution of bromine in alcohol gives a clear liquid, which after concentration to remove most of the alcohol yields when poured into water a white precipitate; this, after drying and crystallising from chloroform, furnishes colourless prisms, m. p. $152\cdot5^\circ$ (decomp.; corr.) (Found: $Br = 49\cdot14$; $C = 26\cdot18$; $H = 1\cdot19$. $C_7H_3O_4NBr_2$ requires $Br = 49\cdot20$; $C = 25\cdot86$; $H = 0\cdot92$ per cent.). Yield 96 per cent. This is proved to be *2:4-dibromo-6-nitro-3-hydroxybenzaldehyde* by the following reactions. On oxidation with alkaline permanganate, it is converted into an acid crystallising from water in colourless, soft needles, m. p. 230° (decomp.; corr.) (Found: $Br = 47\cdot43$. $C_7H_3O_5NBr_2$ requires $Br = 46\cdot89$ per cent.). *2:4-Dibromo-6-nitro-m-cresol*, on oxidation with alkaline permanganate, yields *2:4-dibromo-6-nitro-3-hydroxybenzoic acid* in 10 per cent. yield along with much unoxidised material, which is identical with the acid obtained from the mercury compound. The latter must therefore have the mercury residues in positions 2 and 4.

Shaking the dimercurated compound with a 5 per cent. solution of iodine in potassium iodide causes the mercury to be replaced

by iodine with the formation of *2:4-di-iodo-6-nitro-3-hydroxybenzaldehyde* in almost quantitative yield. This substance crystallises from alcohol in hard, yellow prisms or thick needles, m. p. 142° (decomp.; corr.), which darken on keeping and lose their transparency (Found: I = 61.08. $C_7H_3O_4NI_2$ requires I = 60.60 per cent.). The *semicarbazone* melts at 214° (decomp.; corr.) and the *oxime* at $207-208^\circ$ (decomp.; corr.). In addition, there is sometimes formed a compound which melts at 184° (decomp.; corr.), but the precise conditions for its production have not been determined. It is a *mercuric iodide additive compound* of *2:4-di-iodo-6-nitro-3-hydroxybenzaldehyde* and can also be obtained by mixing the di-iodo-compound (2 mols.) with mercuric iodide (1 mol.) and crystallising the mixture from alcohol, when it separates in soft, yellow needles which darken on keeping (Found: Hg = 16.2. $2C_7H_3O_4NI_2HgI_2$ requires Hg = 15.5 per cent.). Mercuric oxide is not precipitated from this compound by sodium hydroxide solution, but hydrogen sulphide decomposes it, forming mercuric sulphide and *2:4-di-iodo-6-nitro-3-hydroxybenzaldehyde*.

On shaking the crude mono-mercury compound with excess of iodine solution, there is obtained a *mono-iodo-6-nitro-3-hydroxybenzaldehyde*, crystallising from alcohol in short, shining, yellow prisms, m. p. 206° (decomp.; corr.) (Found: I = 44.00. $C_7H_4O_4NI$ requires I = 43.33 per cent.). This mono-iodo-compound also loses its transparency on keeping and after several months becomes almost black in colour. There is also formed a small amount of the di-iodo-compound melting at 142° (decomp.).

When two molecular proportions of mercuric acetate are used for the mercuration, the product consists almost entirely of dimercurated compounds, but the last crops contain a little monomercurated substance, which is difficult to separate, but is proved to be present by the formation of the mono-iodo-compound melting at 206° on treatment with iodine.

4-Nitro-3-hydroxybenzaldehyde, treated by the general method described above, yields an orange-coloured solid consisting wholly of dimercurated compounds, which is filtered off hot. On cooling the filtrate, a mixture of mono- and di-mercurated products separates and on concentration the mother-liquors yield mainly a mono-mercurated product, mixed with unchanged *4-nitro-3-hydroxybenzaldehyde* and a little of the dimercurated compound.

The dimercurated substance from its analysis appears to be a *hydroxymerci-acetoxymerci-4-nitro-3-hydroxybenzaldehyde* (Found: Hg = 62.38. $C_9H_7O_7NHg_2$ requires Hg = 62.47 per cent.). It is insoluble in most organic solvents, but dissolves in hot formic acid, from which, on cooling, pale yellow needles of

2 : 6-diformoxydimercu-4-nitro-3-hydroxybenzaldehyde (the formoxy-mercuri-group = $-\text{Hg}\cdot\text{O}\cdot\text{COH}$) (Found : Hg = 61.62. $\text{C}_9\text{H}_5\text{O}_8\text{NHg}_2$ requires Hg = 61.13 per cent.) crystallise out. On heating, this substance darkens at 120° and explodes at 257° , but does not melt. Boiling with formic acid decomposes it with separation of metallic mercury. The compound is soluble in potassium hydroxide to a deep red solution, from which hydrochloric acid precipitates 2 : 6-dichlorodimercuri-4-nitro-3-hydroxybenzaldehyde. The latter crystallises from alcohol in bundles of minute, pale yellow needles, which darken on heating at 240° , but do not melt at 300° (Found : Hg = 61.32. $\text{C}_7\text{H}_3\text{O}_4\text{NCl}_2\text{Hg}_2\text{H}_2\text{O}$ requires Hg = 61.24 per cent.). The compound loses a molecule of water at 60° in a vacuum and the anhydrous substance decomposes at 282° (corr.). The solution in potassium hydroxide is decomposed by carbon dioxide with precipitation of 2 : 3-anhydro-2 : 6-dihydroxydimercu-4-nitro-3-hydroxybenzaldehyde (Found : Hg = 68.73. $\text{C}_7\text{H}_3\text{O}_5\text{NHg}_2$ requires Hg = 68.92 per cent.).

The mixture of mono- and di-mercurated compounds can be separated into its components by repeated extraction with cold formic acid, in which the mono-compound is the more soluble, precipitation of the mercury compound by addition of ether, and finally crystallisation of each fraction from formic acid (Found : for the mono-compound, Hg = 49.00. $\text{C}_8\text{H}_5\text{O}_6\text{NHg}$ requires Hg = 48.74 per cent. Found : for the di-compound, Hg = 61.63. $\text{C}_9\text{H}_5\text{O}_8\text{NHg}_2$ requires Hg = 61.13 per cent.).

Monoformoxymercuri-4-nitro-3-hydroxybenzaldehyde melts at 233—235° (decomp.; corr.). The mixture containing only a little dimercurated compound is best purified by steam distillation to remove 4-nitro-3-hydroxybenzaldehyde, and crystallisation of the residual mercury compound from propionic acid. Pale orange needles of *propionoxymercuri-4-nitro-3-hydroxybenzaldehyde* are thus obtained (Found : Hg = 45.07. $\text{C}_{10}\text{H}_9\text{O}_6\text{NHg}$ requires Hg = 45.62 per cent.). The solution of this in potassium hydroxide gives on addition of hydrochloric acid a yellow precipitate of *chloromercu-4-nitro-3-hydroxybenzaldehyde*, which decomposes on heating at about 187° (Found : Hg = 50.23. $\text{C}_7\text{H}_4\text{O}_4\text{NClHg}$ requires Hg = 49.89 per cent.). The same products are obtained (the dimercurated compound in predominating amount) when two molecular proportions of mercuric acetate are used for the preparation.

On shaking the dimercurated compound with excess of a freshly prepared, cooled 5 per cent. solution of bromine in alcohol, there is formed in 80 per cent. yield a dibromo-compound, which crystallises from chloroform in colourless prisms, m. p. 152.5° (decomp.; corr.) (Found : Br = 49.25. Calc. for $\text{C}_7\text{H}_3\text{O}_4\text{NBr}_2$, Br = 49.20 per

cent.). This substance shows no depression of melting point on admixture with 2 : 4-dibromo-6-nitro-3-hydroxybenzaldehyde. On oxidation with alkaline permanganate, an acid is formed melting at 230° (decomp.; corr.) which does not depress the melting point of 2 : 4-dibromo-6-nitro-3-hydroxybenzoic acid prepared either from 2 : 4-dibromo-6-nitro-*m*-cresol or from the dimereuri-derivative of 6-nitro-3-hydroxybenzaldehyde (see above).

In the expectation, which as shown above was not realised, that replacement of the two mercury residues in this compound by bromine would yield 2 : 6-dibromo-4-nitro-3-hydroxybenzaldehyde, which could be converted into the corresponding acid, the latter was prepared by oxidation of 2 : 6-dibromo-4-nitro-*m*-cresol with alkaline potassium ferriyanide, which gave rise to two substances, (a) the required acid, 2 : 6-dibromo-4-nitro-3-hydroxybenzoic acid, m. p. 209° (corr.) (Found: Br = 47.23. $C_7H_3O_5NBr_2$ requires Br = 46.89 per cent.), and (b) 4 : 6-dibromo-2-nitrophenol, m. p. 120—121° (Found: Br = 53.91. Cale., 53.84 per cent.); the formation of the latter affords an independent proof of the constitution of the acid.

Treatment of the dimercurated substance with excess of a 5 per cent. solution of iodine in 10 per cent. potassium iodide solution gives rise to a *di-iodo-4-nitro-3-hydroxybenzaldehyde* which crystallises from acetone in yellow needles, m. p. 122° (corr.) (Found: I = 60.91; C = 19.77, 19.98; H = 0.79, 0.74. $C_7H_3O_4NI_2$ requires I = 60.60; C = 20.05; H = 0.72 per cent.). On oxidation with alkaline permanganate, this is converted into a *di-iodo-4-nitro-3-hydroxybenzoic acid*, crystallising from benzene in small, yellow prisms, m. p. 249° (decomp.; corr.) (Found: I = 58.41. $C_7H_3O_5NI_2$ requires I = 58.37 per cent.).

In order to obtain some evidence of the position of the iodine atoms in this substance, 4-nitro-*m*-cresol prepared by Städel and Kolb's method (*Annalen*, 1890, **259**, 210) was treated with iodine and mercuric oxide in aleoholic solution. Under these conditions, it slowly deposits crystals of a *di-iodo-4-nitro-*m*-cresol*, melting at 110° (decomp.; corr.), but the substance is more readily obtained by boiling 4-nitro-*m*-cresol with iodine and iodine acid in dilute aleoholic solution (Found: I = 62.90. $C_7H_5O_3NI_2$ requires I = 62.69 per cent.). 4-Nitro-*m*-cresol on treatment with bromine and mercuric oxide in aleoholic solution gives 2 : 6-dibromo-4-nitro-*m*-cresol (Clause and Hirsch, *J. pr. Chem.*, 1889, [ii], **39**, 61), and by analogy the substance obtained by the action of iodine should be 2 : 6-di-iodo-4-nitro-*m*-cresol. On oxidation with alkaline potassium ferriyanide it is converted into an acid, m. p. 249° (decomp.; corr.), identical with the di-iodo-acid described above,

which should therefore be 2 : 6-di-iodo-4-nitro-3-hydroxybenzoic acid, indicating that the mercury residues in the original dimercuri-compound are in positions 2 and 6, as was expected, since mercury invariably enters in positions ortho or para with respect to the hydroxyl group, which in this series of compounds seems to determine the possibility of mercuration under the conditions described.

The monomercurated compound on treatment with iodine yields a *mono-iodo-4-nitro-3-hydroxybenzaldehyde* crystallising from acetone, or better from chloroform, in shining, yellow needles, m. p. 185° (corr.) (Found : I = 43.37, 43.54. $C_7H_4O_4NI$ requires I = 43.33 per cent.).

In order to remove any doubt as to the purity or identity of the 4-nitro-3-hydroxybenzaldehyde used in the mercuration experiments, it was oxidised, by means of alkaline permanganate, to the known 4-nitro-3-hydroxybenzoic acid, m. p. 235° (corr.), which was also obtained by oxidising 4-nitro-*m*-cresol with alkaline potassium ferricyanide. No trace of any other acid, such as 6-nitro-3-hydroxybenzoic acid, could be detected in the oxidation product of the aldehyde.

Using the general method with 2-nitro-3-hydroxybenzaldehyde (1 mol.) and mercuric acetate (2 mols.), a yellow precipitate forms as the reaction proceeds; this is filtered from the boiling solution from time to time to prevent "bumping." The first crops are amorphous and appear to be *hydroxymercuriacetoxymercuri-2-nitro-3-hydroxybenzaldehyde* (Found : Hg = 62.41. $C_9H_7O_7NHg_2$ requires Hg = 62.47 per cent.). In the later stages, as the concentration of acetic acid increases according to the equation $RH + Hg(O\cdot CO\cdot CH_3)_2 = R\cdot HgO\cdot CO\cdot CH_3 + CH_3\cdot CO_2H$, the solid is deposited in a crystalline condition and consists of *diacetoxymercuri-2-nitro-3-hydroxybenzaldehyde*. Towards the end of the reaction, some reduction of the mercuric acetate takes place and the last crops are contaminated with mercurous acetate.

The product is purified by dissolving it in potassium hydroxide solution, filtering from mercurous oxide, then precipitating with carbon dioxide, and finally crystallising from acetic acid. Pale yellow needles of *diacetoxymercuri-2-nitro-3-hydroxybenzaldehyde* are thus obtained (Found : Hg = 58.35. $C_{11}H_9O_8NHg_2$ requires Hg = 58.62 per cent.). This substance is insoluble in the usual organic solvents, but dissolves in formic, acetic, or propionic acid. It is slightly soluble in sodium hydroxide solution, but comparatively readily soluble in potassium hydroxide solution and from the latter hydrochloric acid precipitates *dichlorodimercuri-2-nitro-3-hydroxybenzaldehyde* as a pale green, gelatinous substance soluble in acetone

or alcohol (Found : Hg = 62.94. $C_7H_3O_4NCl_2Hg_2$ requires Hg = 62.96 per cent.). This decomposes at 236° (corr.).

When one molecular proportion of mercuric acetate is used, the main product is still the dimercurated compound, which separates as already described, but the mother-liquors on concentration deposit a yellow solid consisting of a mixture of mono- and dimercurated products along with unchanged 2-nitro-3-hydroxybenzaldehyde. The solid is finely powdered, thoroughly extracted with ether to remove 2-nitro-3-hydroxybenzaldehyde, and the residual mercury compound fractionally crystallised from acetic acid, in which the mono-compound is the more soluble. Neither the mono- nor the di-acetoxymercu-ri-compound has a definite melting or decomposition point, so that analysis has to be resorted to as a means of controlling the progress of separation. *Acetoxymercu-ri-2-nitro-3-hydroxybenzaldehyde* crystallises from acetic acid in bundles of microscopic needles, which darken on heating, but do not melt at 300° (Found : Hg = 47.43. $C_9H_7O_6NHg$ requires Hg = 47.13 per cent.). The solution in potassium hydroxide on addition of hydrochloric acid gives a pale yellow precipitate of *chloromercu-ri-2-nitro-3-hydroxybenzaldehyde* which decomposes at about 207° (Found : Hg = 49.76. $C_7H_4O_4NClHg$ requires Hg = 49.89 per cent.).

On shaking the dimercurated compound with a slight excess of a cooled, freshly prepared 5 per cent. solution of bromine in alcohol, the mercury is removed and a dibromo-compound is obtained in 88 per cent. yield. This crystallises from chloroform in colourless prisms, m. p. 152.5° (decomp.; corr.) and is identical with the dibromo-compound obtained from the dimercu-ri-derivatives of 6-nitro-3-hydroxybenzaldehyde (p. 1053) and 4-nitro-3-hydroxybenzaldehyde (p. 1055). From the mother-liquors a little 2 : 4-dibromo-6-nitro-3-hydroxybenzoic acid, m. p. 230° (decomp.), is obtained. In this case, as in that of the dimercu-ri-derivative of 4-nitro-*m*-hydroxybenzaldehyde (p. 1056), replacement of the two mercury residues by bromine leads to interchange of position between the nitro-group and the bromine atom in position 6.

Treatment of the dimercu-ri-derivative with excess of a solution of iodine in potassium iodide yields a di-iodo-compound which crystallises from chloroform in bright yellow needles, m. p. 154.5° (corr.) (Found : C = 19.74; H = 0.89; I = 60.27. $C_7H_3O_4NI_2$ requires C = 20.05; H = 0.72; I = 60.60 per cent.).

This di-iodo-compound is not known and the authors have so far been unable to prepare it by this or any other method, which will yield it in sufficient quantity for determination of the position of the iodine atoms. There can, however, be very little doubt that

it is *4 : 6-di-iodo-2-nitro-3-hydroxybenzaldehyde*, since in 2-nitro-3-hydroxybenzaldehyde only three positions (ortho, meta, and para with respect to the hydroxyl) are available for the entry of mercury. As already pointed out, no case is known in which mercury enters in a position meta to hydroxyl, and as two mercury residues enter in this case, it is almost certain that they enter in positions 4 and 6 as suggested in formula III (p. 1050).

The crude monomercurated product on similar treatment yields, together with some di-iodo-compound melting at $154\cdot5^\circ$, a second iodo-compound melting at about 110° which is probably mono-iodo-2-nitro-3-hydroxybenzaldehyde, but owing to the very small quantity available it has not been possible to obtain it in a sufficiently pure condition for analysis.

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